SHORT COMMUNICATION

AgCl and Ag_2S as additives to CuI in Mg–CuI seawater activated batteries

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1. Introduction

The use of silver chloride as a cathode active material in water activated batteries is well known [1]. Silver chloride offers several advantages over other active materials for the cathode because it can be melted, cast into ingots and rolled into sheets upwards of 0.08 mm thick. Since this material is malleable and ductile, it can be used in almost any configuration. Also a base grid need not be used with AgCl. However, its high raw material cost imposes the greatest limitation on its utility in power sources. CuCl, which emerged as an economical alternative to AgCl has the drawbacks of lower energy density, lower rate capability and less resistance to storage at high humidities [2, 3]. Among the other cathode materials developed for Mg-based seawater activated batteries, CuI has superior performance, and the CuI–S blend ranks next to AgCl [4, 5]. The quest continues for the development of a material that will be AgCl equivalent in its performance and, at the same time, cost effective. In the present work AgCl is investigated as an additive to CuI. The effects of light treatment and coaddition of Cu_2S and S to the AgCl–CuI blend are discussed. In addition, Ag_2S is also examined as an additive to AgCl.

2. Experimental details

Cuprous iodide prepared by a reported procedure [6] was dried in air oven at 80 °C and then ground into a fine powder and sieved on a 100 mesh. AgCl was precipitated from nitrate solutions. Ag_2S, Cu_2S and S (99.5%, orthorhombic) were Merck extrapure products. 2.56 g of CuI (0.36 A h) constituted the prime depolarizer, which was uniformly mixed with other additives. The active material was mounted on a thin copper mesh of dimensions 4.0 cm × 2.5 cm × 0.2 cm, wrapped with filter paper and then pressed using a hydraulic press. A compaction pressure of 10 ton was found to give good performance and no binder was used [6]. Two ft long fluorescent tubes (1000 lux) was used for the light treatment of the cathode mix.

The anode was made from magnesium alloy (AZ31) sheets of dimensions 4.0 cm × 2.5 cm × 0.15 cm. The connection for the anode was provided by means of metallic rivets fixed to the magnesium plates. The plates were cleaned with acetone and then with concentrated HCl.

A cathode plate was placed between two magnesium anodes; a pair of thin PVC wires pasted on to the inner side of the magnesium plates prevented direct contact of the cathodes with the anodes [7].

The cell was connected in series to a variable resistor and in parallel to a voltmeter and then immersed in a 100 ml beaker containing 3.3% NaCl as the electrolyte. All the discharges were constant current drains (85 mA) and were carried out at room temperature (25 ± 1) °C. However, the internal resistance of the cell was measured as the slope of the plot of cell voltage against current density.

For the conductivity measurements, the end of discharge product was washed under a stream of water when the lighter colloidal graphite was washed away. It was dried at 80 °C in an oven. After grinding into a fine powder, the product was made into a pellet of 6 mm diameter and 0.2 mm thickness. Electrical contact points were made with gold deposit/silver paint and the conductivity was measured using an assembled Hall and van der Pauw system.

3. Results and discussion

Keeping in mind that the cost of AgCl is about eight times that of CuI and that of Ag_2S is about ten times higher, the present study was restricted to small amounts of AgCl and Ag_2S as additives to CuI.

3.1. *Effect of AgCl*

The AgCl containing cathode mix was subjected to light treatment prior to cathode fabrication. The Mg–CuI battery using this cathode shows a slight increase in cell voltage while the internal resistance of the cell decreases. Further, in the presence of AgCl a lesser quantity of colloidal graphite is adequate to obtain the same performance as that with 15% colloidal graphite in the absence of AgCl. The discharge curves (Fig. 1) show that light treatment of the cathode mix confers advantageous battery characteristics to the cathode. In the deliberately light treated samples AgCl has been reduced to Ag more easily than in the sample normally exposed to the surrounding atmosphere. The results are presented in Table 1.

3.2. *Effect of AgCl + Cu_2S*

The influence of Cu_2S as an additive to CuI in conjunction with AgCl in a 1 : 1 molar ratio is shown in Fig. 2 and Table 1. The idea of putting together AgCl and Cu_2S is based on the fact that Cu_2S is capable of

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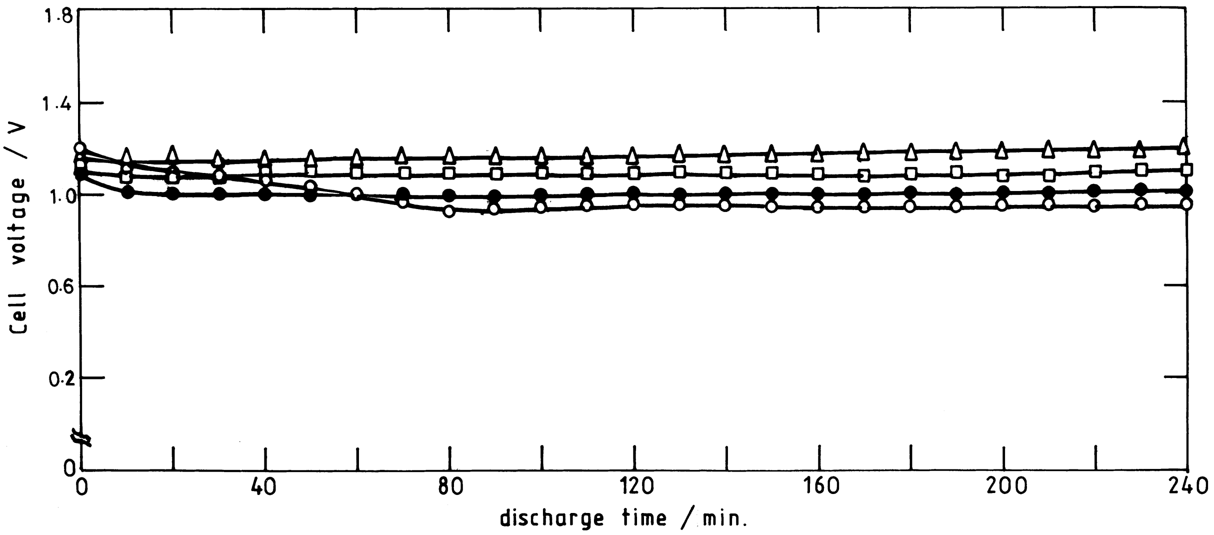

Fig. 1. Effect of Photolysis of AgCl containing CuI on its battery discharge performance. Current drain = 85 mA. Key: (○) 0.50% AgCl not light treated; (●) 0.50% AgCl light treated; (□) 1.25% AgCl light treated; (△) 2.50% AgCl light treated.

reducing AgCl to Ag [8]. The battery performance in this case (Fig. 2) is similar but slightly superior to that of the light treated sample. This is probably due to the fact that Ag is much more dispersed in the cathode mix in the former than in the latter.

An important observation made in this case is that 6% colloidal graphite was adequate to match the performance of a 10% colloidal graphite required for each of the combinations viz., CuI + AgCl and CuI + AgCl + Cu_2S. It seems probable therefore that some Ag_2S is also formed in the electrode reaction. Ag_2S, by virtue of possessing high electrical conductivity, can be expected to enhance the conductivity of the cell, hence lowering internal resistance (Table 1).

Table 1. Effect of additives to CuI in Mg–CuI seawater activated battery

Colloidal graphite	*Cathode composition*				*Cell voltage* /V	*Cell resistance* /nΩ
	AgCl /wt %	*Cu_2S* /wt %	*S* /wt %	*Ag_2S* /wt %		
15.0	0.00	–	–	–	1.08	24.58
10.0	1.25	–	–	–	1.13	20.14
5.0	2.50	–	–	–	1.18	24.71
10.0	2.50	–	–	–	1.20	14.33
5.0	5.00	–	–	–	1.14	16.47
2.5	5.00	–	–	–	1.18	18.94
0.0	5.00	–	–	–	1.13	19.48
10.0	1.25	1.13	0.00	–	1.15	19.00
10.0	1.25	1.13	0.50	–	1.22	18.92
10.0	1.25	1.13	2.00	–	1.38	18.44
10.0	1.25	1.13	3.00	–	1.40	18.00
10.0	1.25	1.13	5.00	–	1.45	17.69
10.0	1.25	1.13	8.00	–	1.52	16.84
10.0	1.25	1.13	10.00	–	1.58	16.23
6.0	1.25	1.13	10.00	–	1.54	19.78
6.0	–	–	0.00	1.25	1.10	17.22
6.0	–	–	0.50	1.25	1.12	17.86
6.0	–	–	2.00	1.25	1.20	18.88
6.0	–	–	3.00	1.25	1.36	19.00
6.0	–	–	5.00	1.25	1.47	22.14
6.0	–	–	8.00	1.25	1.54	18.37
6.0	–	–	10.00	1.25	1.60	20.43

3.3. *Effect of Ag_2S*

Figure 3 shows the effect of Ag_2S on CuI. With 1.25% wt of Ag_2S, 6% colloidal graphite was adequate to produce the same internal resistance value as that of 15% colloidal graphite in the absence of Ag_2S. A point of interest with Ag_2S addition to CuI is that the compacted electrode was very shiny and had a metallic appearance. Ag_2S, which is malleable and ductile and is highly conducting, confers the above good qualities to the CuI + Ag_2S blend.

3.4. *Effect of Ag_2S + S*

The influence of Ag_2S on CuI in the presence of S is also illustrated in Fig. 3. The internal resistance of the cell (Table 1) does not show any regular trend but fluctuates, and the values in most cases are not higher than those in the absence of S. This may be explained on the basis of the fact that though Ag_2S is highly conducting, its conductivity is greatly reduced in the presence of excess sulfur [9].

3.5. *Conductivity measurement*

The preliminary conductivity measurements (Table 2) carried out on the cathode mix materials used in the present study indicate that the end-of-discharge products may be ionic/superionic stoichiometric composites [10–14] comprising AgI, AgCuI, AgCuIS etc. Further experimental studies to ascertain the reaction mechanism, as well as the nature of end of discharge products, are underway.

4. Summary

(i) AgCl has been used in reduced form as an additive to CuI in the Mg–CuI sea water activated battery.

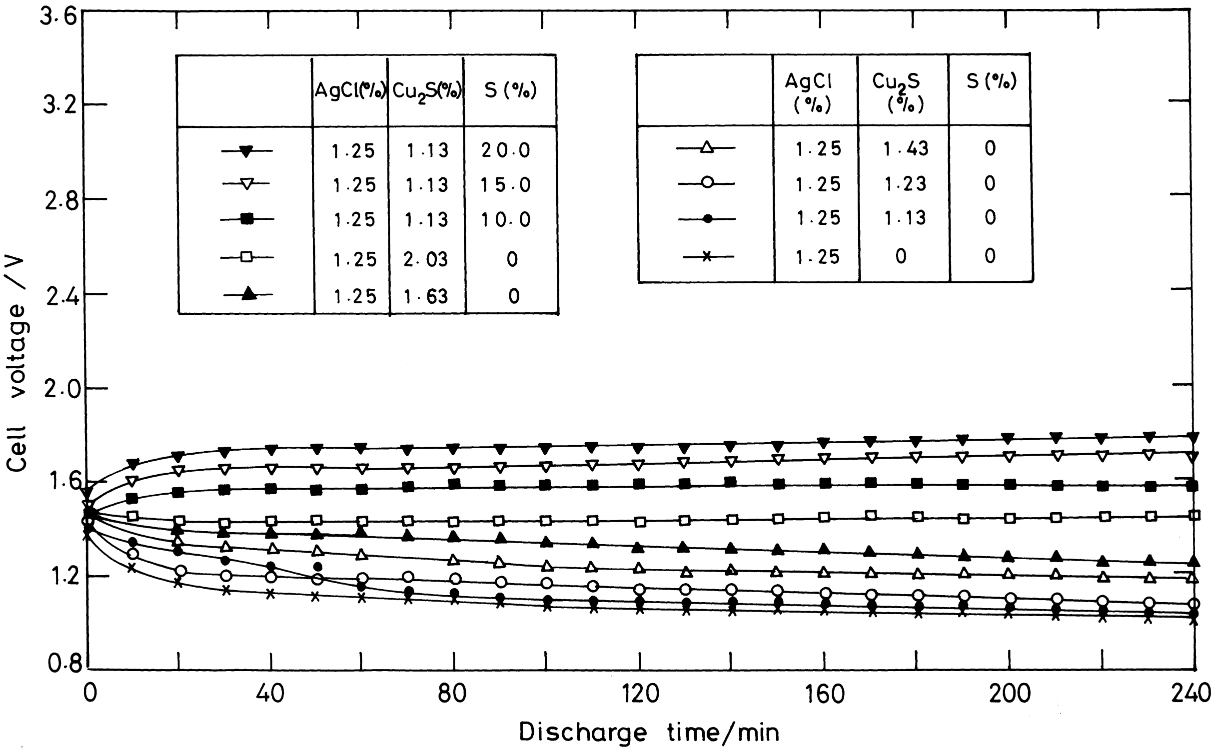

Fig. 2. Effect of AgCl/Cu$_2$S addition on the discharge behaviour of Mg–CuI seawater activated battery. 1.25% : 1.13% is a near 1 : 1 molar ratio of AgCl : Cu$_2$S. The other combinations are included for comparison. Current drain = 85 mA.

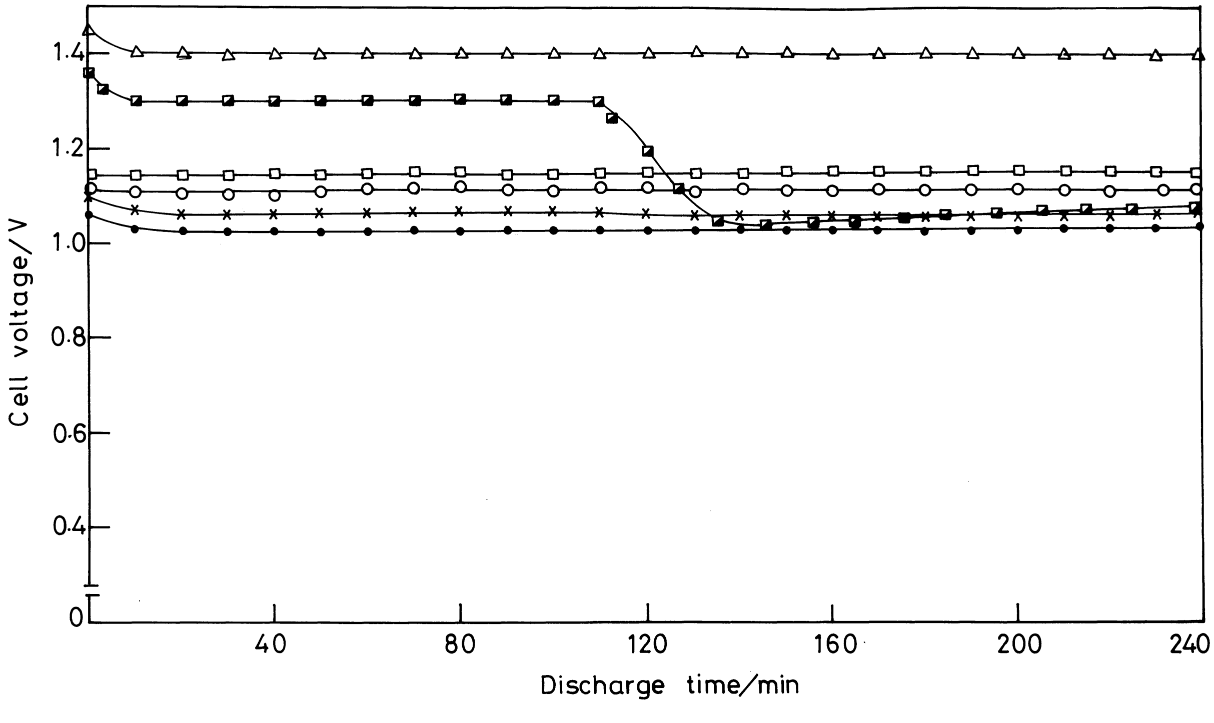

Fig. 3. Effect of Ag$_2$S and S as additives to CuI in Mg–CuI seawater activated battery. Current drain = 85 mA. Key: (●) CuI + 15% colloidal graphite (CG); (×) CuI + 0.25% Ag$_2$S + 15% CG; (○) CuI + 0.50% Ag$_2$S + 10% CG; (□) CuI + 1.25% Ag$_2$S + 10% CG; (◪) CuI + 1.25% Ag$_2$S + 6% CG + 5.0% sulfur; (△) CuI + 1.25% Ag$_2$S + 6% CG + 10% sulfur.

(ii) The reduction of AgCl to Ag has been carried out in the cathode mix by (a) light treatment, and (b) Cu$_2$S treatment.

(iii) Cu$_2$S reduction is found to be superior to photoreduction.

(iv) Voltage increasing effect of S [4, 5] on CuI is facilitated in the presence of AgCl and Cu$_2$S.

(v) Ag$_2$S as an additive to CuI, reduces the internal resistance of the Mg–CuI cell. However, in the presence of S, the internal resistance values do not show any regular trend.

Table 2. Conductivity of end-of-discharge products

Composition of the cathode mix					*Conductivity* /Ω^{-1} cm^{-1}
CuI /g	*AgCl* /wt %	*Cu_2S* /wt %	*S* /wt %	*Ag_2S* /wt %	
2.56	–	–	–	–	$^*3.14 \times 10^{-7}$
2.56	5.00	–	–	–	$^*4.33 \times 10^{-4}$
2.56	2.50	–	–	–	$^*3.12 \times 10^{-5}$
2.56	1.25	–	–	–	$^*6.32 \times 10^{-6}$
2.56	1.25	1.13	–	–	$^*5.32 \times 10^{-4}$
2.56	1.25	1.13	10	–	8.37×10^{-4}
2.56	–	–	–	1.25	6.81×10^{-3}
2.56	–	–	2	1.25	8.01×10^{-3}
2.56	–	–	5	1.25	7.03×10^{-3}
2.56	–	–	7.5	1.25	1.03×10^{-4}
2.56	–	–	10.0	1.25	1.17×10^{-5}
2.56	–	–	10.0	–	4.82×10^{-4}
2.56	1.25	–	10.0	–	6.37×10^{-4}

*These values correspond to the conductivity of undischarged samples.

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